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(54) **Process for the treatment of waste material suspensions.**

(57) There is disclosed a process for treating an aqueous suspension of a particulate waste material, which comprises the step of precipitating an alkaline earth metal carbonate in the said aqueous suspension of the particulate material whereby the said particulate material present at the start of the process becomes entrained in the alkaline earth metal carbonate precipitate. The process described is particularly suited to the treatment of a finely divided particulate material which is an industrial by-product and which is normally difficult to recover by dewatering.

The resultant product finds utility as a filler or pigment for use in paper making or paper coating respectively.

EP 0 604 095 A1

This invention relates generally to a process for the treatment of a suspension of a waste material, such as by-products of wet-mineral refining proc sses and waste waters from paper mills, which have hitherto been found to be difficult to dewater when dispersed in aqueous suspension at low solids. Additionally, this invention relates to the aggregated product of such a process which have advantageous properties when used in paper making and paper coating, or when used as a filler or extender for paints, plastics compositions and the like.

Many naturally occurring mineral materials are subjected to particle size separations in order to select those particles which have the most desirable distribution of sizes for a particular application. In many cases the natural mineral material contains a significant proportion of particles which are undesirably fine for the particular application for which the mineral material is being prepared, and it is necessary to remove these excessively fine particles. When the particle size separation is performed on a mineral material in suspension in a liquid, which would most commonly be water, and when the undesired fine particles have an equivalent spherical diameter of about 0.5μm or less, the suspension of the undesired fine particles is often recovered in the form of a dilute suspension which is extremely difficult to dewater by conventional methods. It is generally unacceptable, for environmental reasons, to allow such dilute suspensions of fine mineral particles to be discharged to rivers or lakes, and, as a result, such unwanted suspensions of very fine particles are often retained in lagoons, thus occupying large areas of land which could more profitably be used for other purposes.

Organic wastes, for example the waste water from a paper mill in which the suspended solid material consists predominantly of cellulosic fibres usually in association with a smaller amount of an inorganic mineral filler, are also environmentally undesirable and difficult to dewater.

It is well known that calcium carbonate of fine particle size can be chemically precipitated by contacting together a source of calcium ions and a source of carbonate ions. The source of carbonate ions may be, for example, carbon dioxide gas in the presence of water or an alkali metal carbonate such as soda ash. TAPPI Monograph Series No. 30, "Paper Coating Pigments", pages 34-35 describes three main commercial processes for preparing precipitated calcium carbonate which is especially suitable for use in the paper industry. In all three processes limestone is first calcined to produce quicklime, and the quicklime is then slaked in water to yield calcium hydroxide or milk of lime. In the first process the milk of lime is directly carbonated with carbon dioxide gas. This process has the advantage that no by-product is formed, and it is relatively easy to control the properties and purity of the calcium carbonate product. In the second process the milk of lime is contacted with soda ash to produce by double decomposition a precipitate of calcium carbonate and a solution of sodium hydroxide. The sodium hydroxide must be substantially completely separated from the calcium carbonate if this process is to be commercially attractive. In the third main commercial process the milk of lime is first contacted with ammonium chloride to give a calcium chloride solution and ammonia gas. The calcium chloride solution is then contacted with soda ash to produce by double decomposition precipitated calcium carbonate and a solution of sodium chloride.

US-A-5082887 describes a process in which an aqueous suspension of fine mineral particles is treated with a high molecular weight carboxyl-containing polymer to flocculate the particles. An excess of calcium ion is then added to precipitate the calcium salt of the carboxyl-containing polymer in situ on the mineral flocs, thus forming aggregates of the mineral particles. Gaseous carbon dioxide is then added to the slurry to react with the remaining calcium ion in the slurry to precipitate calcium carbonate on to the polymeric carboxyl calcium salt.

US-A-3152001 describes a process for the production of a filler in which a calcium carbonate is first precipitated from an aqueous solution and then the surface of the precipitated calcium carbonate is modified by SiO_2. Thereafter, a finely divided silicate is precipitated onto the SiO_2-modified calcium carbonate. The resultant filler is for use as a reinforcing filler for an elastomer.

US-A-2470577 discloses a filler material prepared by precipitating calcium carbonate and calcium silicate simultaneously from a common reaction solution.

According to a first aspect of the present invention there is provided a process for treating an aqueous suspension of a particulate waste material, which comprises the step of precipitating an alkaline earth metal carbonate in the said aqueous suspension of the particulate material whereby the said particulate material present at the start of the process becomes entrained in the alkaline earth metal carbonate precipitate.

The particulate waste material may comprise a particulate inorganic material. The particulate inorganic mineral (when present) is preferably finely divided, by which we mean that it will generally have an average particle diameter smaller than 1μm, and usually smaller than about 0.5μm.

The particulat waste mat rial may alternatively, or in addition to an inorganic component, comprise an organic waste component, for example waste organic fibres (e.g. cellulosic fibres) which typically have a length no greater than 75μm. When th particulate waste material comprises a combination of a particulate inorganic material and an organic waste component such as waste organic fibres (typical of a paper mill waste), the inorganic component will usually make up at least 5% by weight of the total waste material; in some circumstanc-

es, the inorganic component may comprise as little as 2% or as much as 25% by weight of the total waste material.

The aqueous suspension is preferably dilute by which we mean that it contains no more than about 20% by weight of the dry particulate material on a dry weight basis, more preferably less than 10% by weight thereof. Where the waste suspension to be treated is a paper mill waste, the solids concentration thereof is likely to be considerably less than 10%, for example of the order of 1%.

The present invention is particularly suited to the aggregation of a particulate material which is an industrial by-product such as a finely divided kandite clay mineral such as kaolin, a smectite clay such as bentonite, montmorillonite, saponite, hectorite or beidellite, paper mill effluent (which is normally a mixture of cellulose fibres and inorganic fillers). The invention is also suited to the treatment of the slimes produced as a by-product of the beneficiation of phosphate rock such as apatite or of the extraction of diamonds from clay materials of the kimberlite type; such ore enrichment slimes include an inorganic component and occasionally will include also an organic component. When the particulate material is an industrial by-product of this type which is finely divided, for example having an average particle diameter smaller than 1μm, and typically smaller than about 0.5μm, and which exists as an aqueous suspension containing not more than about 10% by weight of dry by-product, the present invention is particularly advantageous because suspensions of these materials are very difficult to dewater. An aqueous suspension of the aggregated product resulting from the process of the present invention is relatively easy to dewater.

The process of the present invention could also be used in the treatment of an organic waste suspension which is difficult to dewater by other methods and which would yield a useful product when co-aggregated with a precipitated alkaline earth metal carbonate.

The particles of the particulate material may have on their surface a polymeric material such as a dispersing agent which was added in a previous separation step. This would have the effect of making a suspension of the particulate material harder to dewater and the present invention, therefore, more advantageous.

The alkaline earth metal carbonate is most preferably a calcium carbonate.

In the process of the present invention, the alkaline earth metal carbonate precipitate may be formed by introducing into the suspension of the particulate mineral a source of alkaline earth metal ions and a source of carbonate ions. This will form the desired precipitate of alkaline earth metal carbonate <u>in situ</u> which will entrain the particulate mineral. The first reagent which is added should preferably be uniformly distributed throughout the aqueous suspension of the particulate material to avoid local concentration gradients. When the first reagent is sparingly soluble, as is the case with calcium hydroxide, thorough mixing is desirable. It is also desirable that the suspension should be agitated while the second reagent is added in order to ensure an even distribution of the precipitate.

It is preferred to add the source of alkaline earth metal ions followed by the source of carbonate ions; when the alkaline earth metal is calcium, this ensures that the scalenohedral form of calcium carbonate is precipitated, which appears to give the best light scattering properties when the aggregated product is to be used in paper making or paper coating.

The source of alkaline earth metal ions is conveniently the alkaline earth metal hydroxide (known as milk of lime when the alkaline earth metal is calcium), but it may alternatively be a water-soluble alkaline earth metal salt, for example the chloride or nitrate. The alkaline earth metal hydroxide may be added to the aqueous suspension already prepared, or may alternatively be prepared in situ, for example by slaking an alkaline earth metal oxide (e.g. quicklime, when an aqueous suspension of calcium hydroxide is desired) in the suspension.

The source of carbonate ions is conveniently carbon dioxide gas which is introduced into the suspension containing the particulate material and the source of alkaline earth metal ions. The carbon dioxide gas may be substantially pure as supplied in gas cylinders or may be present in a mixture of gases such as flue gases. Alternatively, the source of carbonate ions may be an alkali metal or ammonium carbonate. Sodium carbonate is especially preferred on account of its relative cheapness and availability.

When the process of the present invention is used for the treatment of a suspension of an organic waste, for example for the treatment of waste water from a paper mill, in which the suspended solid material consists predominantly of cellulosic fibres, the source of alkaline earth metal ions may be introduced into the suspension, either by slaking an alkaline earth metal oxide, for example calcium oxide or quicklime, in the suspension, or by adding to the suspension a separately prepared suspension of an alkaline earth metal hydroxide.

Whether the alkaline earth metal oxide is slaked in waste water or in fresh wat r, the water may be at ambient temperature, but is preferably heated to a temperature in th range from 40°C to 50°C, and the suspension of th alkaline earth metal oxide in the water is pref rably agitated vigorously for a time of up to 30 minutes to ensure that the slaking is complete.

The quantity of the source of alkaline earth metal ions and the source of carbonate ions used is preferably such as to precipitate sufficient alkaline earth metal carbonate to increase the dry solids content of the aqueous

suspension to within the range from 10% to 20% by weight. The weight ratio of fine mineral to alkaline earth metal carbonate (preferably calcium carbonate) will depend upon the nature of the fine mineral. For example bentonite may need at least 80% by weight of the mixture to be alkaline earth metal carbonate, while, in the case of fine kaolinite, only about 25% by weight of th mixture may need to be alkaline earth metal carbonate to give acceptable dewatering.

The suspension containing the precipitate of alkaline earth metal carbonate (preferably calcium carbonate) and entrained particulate material (e.g. an industrial by-product) may be added directly in its relatively dilute form to a paper making composition to provide filler particles for the paper making fibres. Alternatively the suspension may be dewatered by any conventional method, for example by pressure filtration or in a centrifuge.

If desired, a reducing bleaching agent may be added to the suspension containing the particulate material or by-product in order to improve its whiteness. The reducing bleaching agent may be, for example, a dithionite salt, such as sodium or zinc dithionite, or zinc dust and sulphur dioxide. The amount of the reducing bleaching agent used is preferably in the range from 1.5 to 7.5 grams of the reducing bleaching agent per kilogram of dry particulate material. The bleaching agent could be added after the addition of the first reagent, but before addition of the second reagent.

The suspension of the precipitate of alkaline earth metal carbonate and entrained particulate material is found to be very much easier to dewater than the original suspension of the particulate material alone, because, when a cake of the mixed solid material is formed by filtration or by centrifuging, the packing of the particles is such that the cake is very much more permeable to water than is a cake of the particulate material by-product alone. Also the mixed solid material is found to give advantageous light scattering properties when used as a paper filler material or as a paper coating pigment.

According to a second aspect of the present invention there is provided a composite mineral pigment/filler comprising aggregates consisting essentially of precipitated alkaline earth metal carbonate (preferably calcium carbonate) and a particulate material, the particles of which are entrained in the alkaline earth carbonate precipitate. Such aggregates can be used in the preparation of a paper-making composition or a paper-coating composition. A paper making composition will contain, in aqueous suspension, and in addition to the aggregated filler of the invention (and optionally other filler materials), cellulosic fibres and other conventional additives known in the art. A typical paper making composition would contain up to about 67% by weight of dry filler material, based on the dry weight of the paper making fibres, and may also contain a cationic or an anionic retention aid in an amount in the range from 0.1 to 2% by weight, based on the dry weight of the filler material. It may also contain a sizing agent which may be, for example, a long chain alkylketene dimer, a wax emulsion or a succinic acid derivative. The composition may also contain dye and/or an optical brightening agent. A paper coating composition will contain, in aqueous suspension, and in addition to the aggregated pigment of the invention (and optionally other filler materials), an adhesive. The formula of the paper coating composition will depend upon the purpose for which the coated paper is to be used, i.e. either for offset or gravure printing. Generally speaking, the amount of adhesive will be in the range from 3 to 35% by weight of adhesive solids, based on the dry weight of the coating pigment. There will also be present from 0.01 to 0.5% by weight, based on the dry weight of the coating pigment, of a dispersing agent. Sufficient alkali will generally be added to raise the pH to about 8-9. The adhesive solids may be a starch, a water dispersible synthetic resin or latex such as a styrene butadiene copolymer, a polyvinyl alcohol an acrylic polymer, polyvinyl acetate, a butadiene-acrylonitrile copolymer, a cellulose derivative such as methyl cellulose, sodium carboxymethyl cellulose or hydroxyethyl cellulose or a proteinaceous material such as casein, animal glue or a vegetable protein.

The invention will now be illustrated by reference to the following Examples.

EXAMPLE 1

Quicklime (252g) was added to 4,500cm³ of an aqueous suspension at a temperature of 50°C containing 7.5% by weight of kaolin clay particles of average particle size 0.22μm. The suspension was stirred vigorously for 25 minutes to ensure adequate slaking of the quicklime. The pH of the suspension was then found to be 12.5.

There was then introduced into the suspension of clay particles and calcium hydroxide a gas mixture containing 25% by volume of carbon dioxide at a rate of 5,242 $cm^3.min^{-1}$, which corresponds to 0.013 moles of carbon dioxide per minute per mole of calcium hydroxide. The gas mixture was introduced into the suspension as a fine str am of bubbles and vigorous stirring was maintained throughout the introduction.

The pH of the suspension was continuously monitored and the introduction of the gas mixture was continued until the pH of the suspension had fallen to below 8.0.

The particulat component of the resultant suspension which contained 54% by weight of calcium carbon-

ate was examined by means of an electron microscope and was found to comprise a co-aggregated mixed mineral (see the Figure in which the platy particles are the kaolinite and the white "fluffy" particles are the precipitated calcium carbonate).

EXAMPLE 2

The experiment described in Example 1 was repeated several times there being added in each case to the suspension of kaolin clay particles a different amount of the quicklime such that the composition of the mixed mineral produced varied in the range from 35% to 73% by weight of calcium carbonate. As a control, a further suspension was prepared by slaking 252g of quicklime in 4,500cm³ of water which was free of kaolin particles. In each case there was introduced into the suspension 0.013 moles of carbon dioxide per minute per mole of calcium hydroxide.

The suspension of the mixed mineral produced in each case was filtered and the cake of mixed mineral was remixed with water to form a suspension containing 30% by weight of dry mixed mineral, which suspension was used to measure the Kubelka-Munk scattering coefficient, S, by the following method:

A sheet of synthetic plastics paper material, sold by Arjo Wiggins Appleton plc under the Registered Trade Mark "SYNTEAPE", was cut into a number of pieces each of size 10cm x 6cm, and each piece was weighed and tested for percentage reflectance to light of wavelength 457nm when placed over a black background by means of an "ELREPHO" spectrophotometer to give the background reflectance R_b. The preweighed pieces of plastics paper were then coated with different amounts of the suspension of mixed mineral to give coat weights in the range from 5 to 20g.m^{-2}. Each coating was allowed to dry in the air and the area of dry coating on each piece of plastics paper was standardised by placing a circular template over the coating and carefully removing surplus coating which lay outside the periphery of the template. Each piece of plastics paper bearing a coated area was then reweighed, and, from the difference in weight and the dimensions of the coated area, the coat weight X in kg.m^{-2} was calculated.

Each coated area was then tested for reflectance to light of wavelength 457nm when the piece of plastics paper was placed (a) on a black background (R_0); and (b) on a pile of uncoated pieces of the plastics paper (R_1). Finally the reflectance to light of wavelength 457nm was measured for the pile of uncoated pieces alone (r).

From these measurements the reflectance R_c of the coating alone was calculated from the formula:-

$$R_c = \frac{R_1.R_b - R_0.r}{(R_1 - R_0).rR_b + Rb - r}$$

and the transmission T_c of the coating from the formula:-

$$T_c^2 = \frac{(R_0 - R_c)(1 - R_cR_b)}{R_b}$$

From these two quantities it is possible to calculate a theoretical value for the reflectance R_{oo}, of a coating layer of infinite thickness of the same material from the formula:-

$$\frac{1 - T_c^2 + R_c^2}{R_c} = \frac{1 + R_{oo}2}{R_{oo}}$$

The Kubelka-Munk scattering coefficient S in m^2.kg^{-1} may now be calculated from the formula:-

$$SX = \frac{1}{b}\coth^{-1}.\frac{1 - aR_c}{bR_c}$$

where

$$a = \frac{1}{2}\left[\frac{1}{R_{oo}} + R_{oo}\right]$$

and

$$b = \frac{1}{2}\left[\frac{1}{R_{oo}} + R_{oo}\right]$$

The scattering coefficient S was plotted against the coat weight X and the value of S in each case for a

coat weight of $8 g.m^{-2}$ was found by interpolation.

The results obtained are set forth in Table 1.

Tabl 1

weight % calcium carbonate	scattering coefficient S
35	227
54	265
73	276
100	253

EXAMPLE 3

The experiment described in Example 1 was repeated except that there was added to the suspension of kaolin clay particles, before the quicklime, 1.69g of sodium dithionite as a reducing bleaching agent. The particulate component of the suspension on completion of the treatment with carbon dioxide gas was separated by filtration and dried in an oven for 16 hours at 80°C. The resultant dry cake was pulverised and the reflectances to light of wavelength 457nm and 570nm, respectively, were measured by means of an "ELREPHO" spectrophotometer.

The experiment was repeated except that no sodium dithionite was added to the suspension of kaolin clay particles.

The results obtained are set forth in Table 2 below:

Table 2

	% reflectance to light of wavelength	
	457nm	570nm
with sodium dithionate	89.9	94.6
without sodium dithionate	88.8	94.2

EXAMPLE 4

The experiment described in Example 1 was repeated several times there being added in each case to the suspension of kaolin clay particles a different amount of the quicklime such that the composition of the mixed mineral produced varied in the range from 0.5% to 99.5% by weight of calcium carbonate. In each case there was introduced into the suspension 0.013 moles of carbon dioxide per minute per mole of calcium hydroxide.

A small sample of the suspension of the mixed mineral produced in each case was poured into a Buchner filter funnel provided with a piece of standard filter paper, the side arm of the filtrate flask being connected to the laboratory vacuum source. The filtrat was collected in a measuring cylinder inside the filtrate flask, and at intervals the volume of filtrate collected and the time which had elapsed since the start of filtration were record d. The square of the volume collected was plotted graphically against the lapsed time, and a curve was obtained which had a large c ntral straight line portion. The slope of this straight line portion was recorded in each case.

The relationship between the square of the volume of filtrate collected and the elapsed time is given by

the Carmen-Kozeny equation:-

$$\frac{Q^2}{T} = \frac{2.A^2.P.E^3.(y - 1)}{5.v.S^2.(1 - E^2).d^2}$$

where:

Q is the volume of filtrate collected;
T is the elapsed filtration time;
A is the area of the filter medium;
P is the differential pressure across the filter medium;
E is the fraction of voidage in the filter cake;
v is the viscosity of the suspending medium;
S is the specific surface area of the particulate phase; and
d is the specific gravity of the particulate phase.

The slope Q^2/T of the straight line portion of the graph plotted for each suspension gave a measure of the filtration rate in each case and, since A, P, v, S and d can be assumed to be constant under the conditions of the experiment, a standardised filtration rate F can be found to be given by:

$$F = \frac{Q^2.R}{T}$$

where:

$$R = \frac{\frac{1}{d} + \frac{W_c}{S_c}}{\frac{W_s}{S_s} - \frac{W_c}{S_c}}$$

where:

W_c is the weight fraction of water in the cake;
S_c is the weight fraction of solids in the cake;
W_s is the weight fraction of water in the suspension; and
S_s is the weight fraction of solids in the suspension.

Suspensions were also prepared by mixing with 4,500cm^3 of the suspension of fine kaolin clay particles different quantities of precipitated calcium carbonate which had been prepared separately from the kaolin clay suspension by carbonating milk of lime. The filtration rate for each mixed suspension and the percentage by weight of dry material in the cake were measured as described above.

The results obtained are set forth in Table 3 below:

Table 3

% by weight of precipitated calcium carbonate in mixture	Precipitated in situ		Separately mixed	
	Filtration rate (F)	% by wt. solids	Filtration rate (F)	% by wt. solids
0	0.001	73.8	0.001	73.8
35	0.380	42.7		
50			0.167	55.9
54	1.090	38.1		
100	7.880	35.4	7.880	35.4

These results show that, for a given percentage by weight of precipitated calcium carbonate in the mixtur , a higher filtration rate is obtained if the calcium carbonate is precipitated in the presence of the fine kaolin than if it is precipitated separately and then added to the suspension of fine kaolin.

EXAMPLE 5

Different quantities of quicklime were added to 4,500cm^3 portions of an aqueous suspension at a temperature of 50°C containing 7.5% by weight of Wyoming sodium bentonite particles of average particle size

smaller than 0.1μm. In each case the suspension was stirred vigorously for 25 minutes to ensure adequate slaking of the quicklime.

There was then introduced into each suspension of bentonite particles and calcium hydroxide a gas mixture containing 25% by volume of carbon dioxide at a rate of 0.013 moles of carbon dioxide per minute per mole of calcium hydroxide. The gas mixture was introduced into the suspension as a fine stream of bubbles and vigorous stirring was maintained throughout the introduction. The pH of the suspension was continuously monitored and the introduction of the gas mixture was continued until the pH of the suspension had fallen to below 8.0.

The filtration rate, F, and the percentage by weight of water retained in the filter cake were measured for each suspension as described in Example 4 above. The results obtained are set forth in Table 4 below:-

Table 4

% by wt. of precipitated calcium carbonate in mixture	Filtration rate (F)	% by wt. solids
80	0.070	43.7
95	1.510	41.5
99	2.140	44.0
100	7.880	35.4

These results show that, when the amount of calcium carbonate precipitated in the suspension is about 90% or more of the total weight of dry bentonite and calcium carbonate, the suspension can be dewatered by filtration at a very advantageous rate, but even when the proportion of calcium carbonate in the mixture is 80% by weight, the rate of filtration would be acceptable in a commercial process.

EXAMPLE 6

11.25g of quicklime was added to 1000ml of an aqueous suspension containing 180g of a kaolin clay having a particle size distribution such that 80% by weight consisted of particles having an equivalent spherical diameter smaller than 2μm. The solids content of the kaolin clay suspension before the addition of the quicklime was 16.2% by weight. The suspension was maintained at a temperature of 50°C and vigorously stirred for 25 minutes to ensure adequate slaking of the quicklime.

A gas mixture comprising 25% by volume of carbon dioxide was then introduced into the suspension as a fine stream of bubbles at a rate of 0.13 moles of carbon dioxide per minute per mole of calcium hydroxide. The temperature of the suspension was maintained at 45°C and the gas mixture was introduced with continuous agitation of the suspension until the pH of the suspension had fallen to below 8.0.

The experiment described above was repeated three more times except that 11.25g of quicklime was added to 1000ml of an aqueous suspension containing, respectively, 60g, 20g and 6.7g of the kaolin clay. The solids content of the suspension of kaolin clay in each case before the addition of the quicklime was, respectively, 16.2%, 5.8%, 2.0% and 0.7% by weight.

A suspension was also prepared containing 180g of the kaolin clay alone in 1000ml of the suspension. A further suspension was prepared by adding quicklime to 1000ml of water and carbonating the calcium hydroxide thus formed under the conditions described above.

The filtration rate, F, and the percentage by weight of water retained in the filter cake were measured for each suspension as described in Example 4 above. The results obtained are set forth in Table 5 below:-

Table 5

% by wt. of precipitated calcium carbonate in mixture	% by wt. of solids in kaolin suspension	Filtration rate (F)	% by wt. of solids in cake
0	16.2	0.06	66.9
10	16.2	0.21	58.1
25	5.8	0.61	50.1
50	2.0	0.93	49.4
75	0.7	1.38	44.7
100	0	2.54	40.1

EXAMPLE 7

A sample of waste water from a paper mill was found to contain 0.27% by weight of suspended solids which were predominantly cellulosic fibres, but also contained a smaller proportion of inorganic filler particles. There were added to three portions of this waste water, each of 1 litre, 14g, 28g and 56g, respectively of quicklime. The mixtures of waste water and quicklime were stirred vigorously at a temperature of 45°C to complete the slaking of the quicklime.

A gas containing 25% by volume of carbon dioxide, the remainder being air, was admitted into each of the portions of suspension at a rate which was calculated to complete the conversion of all the calcium hydroxide present into calcium carbonate in a time of 75 minutes. In each case the temperature of the suspension during carbonation was maintained at 45°C.

Each sample of suspension was filtered and the filtration rate was determined by the method described in Example 4. As a comparison the filtration rate was also determined for a sample of the untreated waste water. The results are set forth in Table 6 below:

Table 6

Volume of quicklime added (ml)	nil	14	28	56
Wt. $CaCO_3$ (g/l)	nil	25	50	100
Waste water solids (g/l)	2.75	2.75	2.75	2.75
% by wt. pptd. $CaCO_3$ in product	nil	90.1	94.8	97.3
CO_2-containing gas rate (ml/m)	-	300	600	1200
CO_2 rate (ml/m)	-	75	150	300
Filtration rate	0.0176	3.0	3.4	6.1

Each of the three products which contained precipitated calcium carbonate were examined under the scanning electron microscope, and were found to consist of fine scalenohedral precipitated calcium carbonate in conjunction with the particles and fibres which were originally present in the waste water

EXAMPLE 8

A further sampl of waste water from a paper mill was weighed and filtered and th residue dried at 110°C. The solids content of the waste water was found to be 0.3% by weight. The dried residue was heated in a furnace for 1 hour at 1000°C and the ignit d residue was weighed again. The loss in weight on ignition of the dry residue was found to b 89% which was accounted for principally by the cellulosic fibre content of the dry residu . It was known that the inorganic fill r used in the paper making process employ d by the mill from which the waste water was recovered consist d predominantly of calcium carbonat , and it was therefore assumed

that the ignited residue, which accounted for 11% of the weight of the dry residue, was calcium oxide. This corresponded to 19.6% by weight of calcium carbonate, and it was therefore estimated that the approximate composition of the solids component of the waste water was 80% by weight of cellulosic fibres and 20% by weight of calcium carbonate.

A suspension of calcium hydroxide was prepared by slaking 112g of quicklime in 1 litre of water at 50°C with vigorous agitation for 25 minutes. Assuming that the quicklime is completely slaked, each litre of suspension prepared in this way will contain 148g of calcium hydroxide.

There were added to three separate 1 litre portions of the waste water, quantities of the calcium hydroxide suspension which were calculated to give, after carbonation with carbon dioxide- containing gas, precipitates which contained, respectively, 60%, 80% and 90% by weight of precipitated calcium carbonate. The gas contained 25% by volume of carbon dioxide, the remainder being air, and the gas was introduced into the mixture of calcium hydroxide suspension and waste water at a rate such as to complete the precipitation in 5 minutes.

Each of the three portions of treated waste water was filtered and the filtration rate was determined by the method described in Example 4. As a comparison, the filtration rate was also determined for a sample of untreated waste water. The results are set forth in Table 7 below:

Table 7

Volume of $Ca(OH)_2$ added (ml)	nil	22.3	59.8	134.0
Wt. of $Ca(OH)_2$ added (g/l)	nil	3.3	8.9	19.8
Wt. calcium carbonate (g/l)	nil	4.5	12.0	26.8
Waste water solids (g/l)	3.0	3.0	3.0	3.0
% by wt. pptd.$CaCO_3$ in product	nil	60	80	90
CO_2-containing gas rate (ml/m)	-	806	2150	4836
CO_2 rate (ml/m)	-	202	538	1209
Filtration rate	0.0048	0.133	0.98	2.43

It can be seen that the filtration rate of the waste water is greatly increased when calcium carbonate is precipitated in the waste water in accordance with the invention.

The filter cake which was obtained by filtering the waste water in which 90% by weight of the solid component consisted of precipitated calcium carbonate was dried and pulverised and the resultant pulverised material used as a filler in a paper making composition.

Hand sheets of paper filled with the composite material prepared as described above were prepared in the following way. 400g of bleached sulphite spruce pulp were soaked in 10 litres of filtered water for 4 hours and the mixture was then disintegrated for 10 minutes in a turbine mixer, the impeller rotating at a speed of 1500rpm. The contents of the mixer were washed out with a further 10 litres of water and transferred to a laboratory beater where a further 2 litres of water was added and the mixture beaten for 16½ minutes. At this stage the stock contained approximately 1.8% by weight of dry pulp. The beating time was chosen to give the optimum compromise between brightness and strength properties of the stock which corresponds to a Canadian Standard Freeness of 300. 800ml of the stock was then made up to 2 litres with water and disintegrated in a laboratory disintegrator which was operated for 15,000 revolutions of the impeller. The volume of stock was made up to 4 litres with filtered water and the consistency was checked by forming a paper sheet from a small sample by draining on a suitable wire screen and drying and weighing the sheet thus formed. Water was added if necessary to reduce the consistency to 0.3% by weight of dry pulp.

The paper making stock thus formed was divided into three portions and a different amount of the pulverised composite filler was added to each portion and stirred in by hand.

Hand sheets were prepared from each of the three portions of filler-containing paper making stock according to the procedure laid down in TAPPI Standard No. T205 om-88, "Forming handsheets for physical tests of pulp". For each hand sheet 400ml of the stock was pour d into the she t forming machine and surplus water was removed.

The ash, or inorganic material, cont nt of the paper formed from each of the three portions of stock was determined by incinerating a sample of paper formed from the stock according to the procedure laid down in TAPPI Standard No. T413 om-85.

The brightness, or percentage reflectance to violet light of the paper formed from each of the three portions of stock was measured by means of a DATACOLOR 2000 brightness meter fitted with a No. 8 filter (457nm wavelength).

The opacity of each sample of paper was measured by means of the DATACOLOR 2000 brightness m ter fitted with a No. 10 filter (a green filter embracing a broad spectrum of wavelengths). A measurement of the percentage of the incident light reflected was made with a stack of ten sheets of paper over the black cavity (R_∞). The ten sheets were then replaced with the single sheet from the top of the stack over the black cavity and a further measurement of the percentage reflectance was made (R). The percentage opacity was calculated from the formula:

$$\text{Percentage opacity} = 100.R/R_\infty$$

The procedure was performed a total of ten times with each time a different sheet of paper on the top of the stack, and the average value of the percentage opacity was determined.

The Kubelka-Munk scattering coefficient, S, for each sample of paper was determined by the procedure described in Example 2 except that, in each case, samples of the paper produced in the manner described above were substituted for the pieces of coated synthetic plastics paper material which were referred to there. The measurements were made using the DATACOLOR 2000 brightness meter fitted with a No. 8 filter.

The hand sheets from each batch were also tested for bursting strength by the test prescribed in TAPPI Standard No. T403 om- 85. The bursting strength is defined as the hydrostatic pressure in kilopascals required to produce rupture of the material when the pressure is increased at a controlled constant rate through a rubber diaphragm to a circular area of the paper 30.5mm in diameter. The area of the material under test is initially flat and held rigidly at the circumference but is free to bulge during the test. Samples of each sheet were also weighed dry, the weight of the dry sample being used to determine the weight per unit area of the paper in grams per square metre. The burst strengths were divided by the weight per unit area of the paper to give a burst ratio.

As a comparison, the experiment described above was repeated, but using as the filler in the paper making composition a proprietary precipitated calcium carbonate product produced by John & E. Sturge Limited under the trade name "CALOPAKE F". The particle size distribution of this material was such that the weight median particle diameter was 3.0μm. The amounts of this proprietary filler used in each of the three portions of paper making stock were intended to be, as nearly as possible, the same as the amounts of the composite filler used in the three portions of stock in the experiment described above.

As a further comparison, hand sheets were prepared from paper making stock which contained no filler and subjected to the same tests as are described above.

The results are set forth in Table 8 below.

Table 8

Filler	Ash	Reflectance (%)	Opacity (%)	Scattering Coefficient S ($cm^2.g^{-1}$)	Burst index
None	0.7	82.2	70.2	288	2.43
CALOPAKE F	6.2	86.4	82.0	545	1.52
	11.2	87.8	85.7	696	1.04
	17.2	89.2	88.3	866	0.60
Composite filler material	6.6	83.1	84.3	537	1.55
	12.0	84.1	89.8	750	0.95
	16.2	84.8	92.6	917	0.60

It will be noted that, although the brightness of the filled paper obtained with the composite filler material is slightly poorer than that obtained with the proprietary pr cipitated calcium carbonate, th opacity and the scatt ring coefficient ar both better in the case of the composite filler material and the burst strength is about the same. The brightness of the composite filler material could be improved by the use of a reducing bleaching agent as described in Example 3 abov .

Claims

1. A process for treating an aqueous suspension of a particulate waste material, which comprises the step of precipitating an alkaline earth metal carbonate in the said aqueous suspension of the particulate material whereby the said particulate material present at the start of the process becomes entrained in the alkaline earth metal carbonate precipitate.

2. A process according to claim 1, wherein the particulate waste material comprises a particulate inorganic material.

3. A process according to claim 2, wherein the particulate inorganic material has an average particle diameter smaller than about 1μm.

4. A process according to claim 3, wherein the particulate inorganic material has an average particle diameter smaller than about 0.5μm.

5. A process according to any one of claims 1 to 4, wherein the particulate waste material comprises an organic waste component.

6. A process according to claim 5, wherein the organic waste component comprises waste organic fibres having a length no greater than 75μm.

7. A process according to any preceding claim, wherein the aqueous suspension contains no more than about 20% by weight of the dry particulate material on a dry weight basis, preferably less than 10% by weight of the dry particulate material on a dry weight basis.

8. A process according to any preceding claim, wherein the particulate material is an industrial by-product selected from the group consisting of: a finely divided kandite clay mineral, a smectite clay such as bentonite, montmorillonite, saponite, hectorite or beidellite, paper mill effluent and the slimes produced as a by-product of the beneficiation of a phosphate rock or of the extraction of diamonds from clay materials of the kimberlite type.

9. A process according to any preceding claim, wherein the alkaline earth metal carbonate is a calcium carbonate.

10. A process according to any preceding claim, wherein the alkaline earth metal carbonate precipitate is formed by introducing into the suspension of the particulate mineral a source of alkaline earth metal ions and a source of carbonate ions.

11. A process according to claim 10, wherein the source of alkaline earth metal ions is chosen from the alkaline earth metal hydroxide and water-soluble alkaline earth metal salts.

12. A process according to claim 10 or 11, wherein the source of carbonate ions is carbon dioxide gas or an alkali metal or ammonium carbonate.

13. A process according to claim 10, 11 or 12, wherein the quantity of the source of alkaline earth metal ions and the source of carbonate ions used is such as to precipitate sufficient alkaline earth metal carbonat to increase the dry solids content of the aqueous suspension to within the range from 10% to 20% by weight.

14. A composite mineral pigment/filler comprising aggregates consisting essentially of precipitated alkalin earth metal carbonate and a particulate waste material, the particles of which are entrained in the alkaline earth carbonate precipitate.

15. A paper making composition comprising, in aqueous suspension, an aggregated filler as claimed in claim 14 or as prepared in any one of claims 1 to 13 and cellulosic fibres.

16. A paper coating composition comprising, in aqueous suspension, an aggregated pigment as claimed in claim 14 or as prepared in any one of claims 1 to 13 and an adhesive.

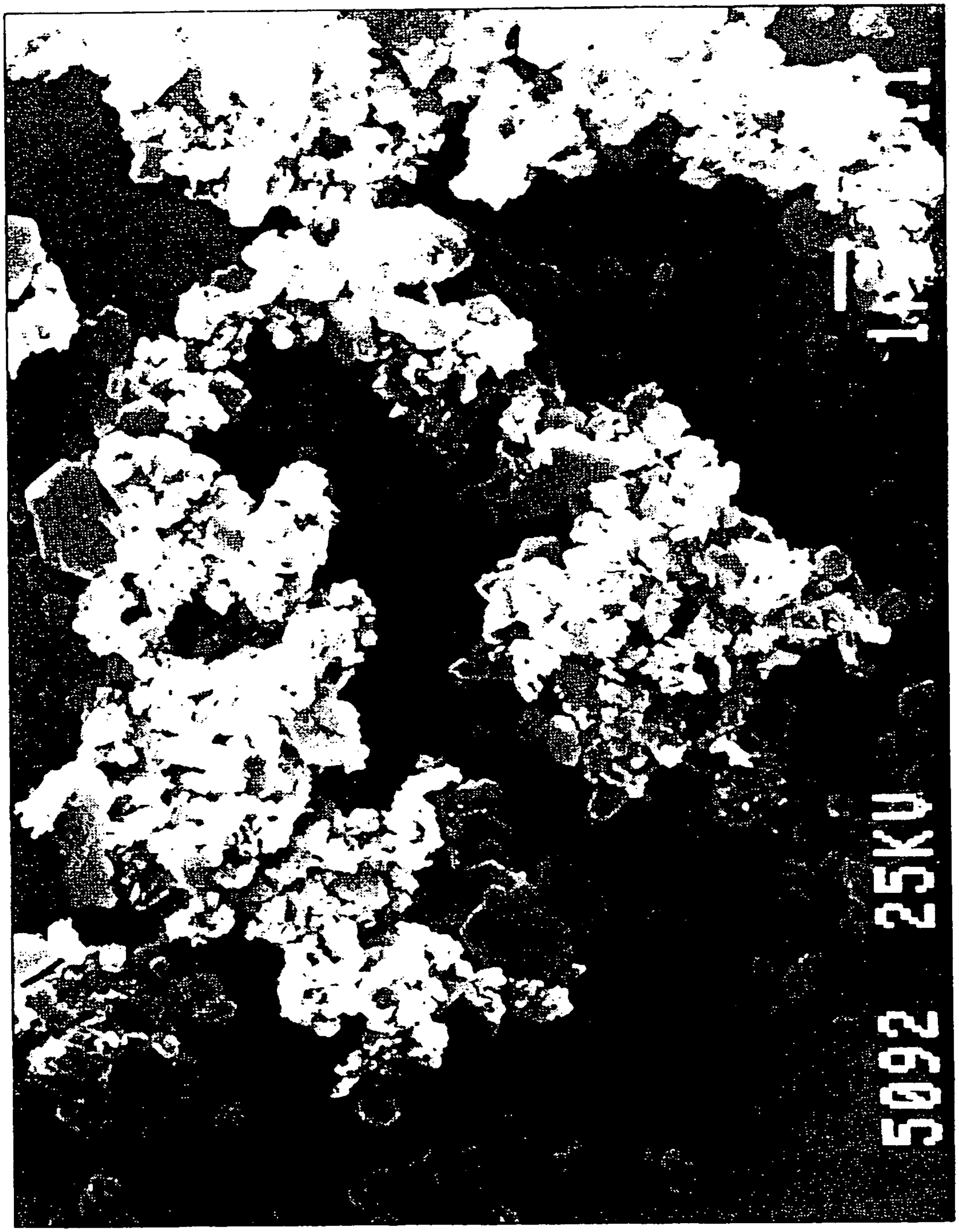

FIG. 1